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cis- AND *trans*-1,2-DIMETHYLSPIRO[2.6]NONA-4,6,8-TRIENE[1]

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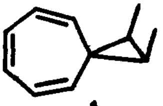
THE DELICATE balance of the norcaradiene-cycloheptatriene equilibrium is of continuing concern to organic chemists.[3] One of the several factors which influence this equilibrium is the magnitude of the external angle at the 7 position of the cycloheptatriene ring. Our interest in this problem[4,5] has led us to attempt a synthesis of a series of compounds in which the external angle is gradually widened. We describe here two molecules, **1** and **2**, in which the external angle is at a minimum, and some remarkable chemical shift coincidences in the nmr spectra of these compounds and their immediate precursors.



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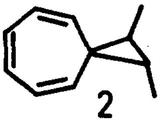

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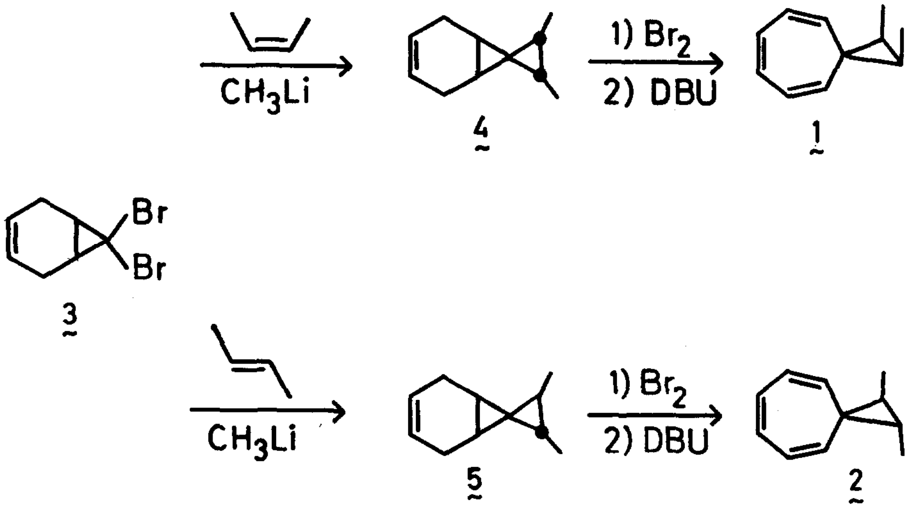
The lone spirononatriene of this type has been described only briefly by Mukai, *et al.*[6] and Jones and Ennis.[7] More important the method of synthesis does not lend itself to the production of a great variety of such compounds and we have therefore attempted to develop a more general route. We seized upon the earlier reports of Moore and Ward,[8,9] that spiropentanes could be produced by the action of methyllithium on olefinic solutions of 7,7-dibromonorcarane and hoped to extend this procedure to 7,7-dibromonorcar-3-ene (**3**). Happily, treatment of this compound in a variety of olefins affords spiropentanes in about 30% yield. In particular, **4** and **5** can be made from *cis*- and *trans*-2-butene respectively. The reaction is at least 99% stereospecific, but the products are accompanied by the compound formed by replacement of one bromine atom of **3** with a methyl group and by the product



of insertion into the α carbon-hydrogen bond of solvent ether.[10] These last two compounds are analogous to ones found by Moore and Ward.

Elemental analysis confirmed that 4 and 5 were of the empirical formula $C_{11}H_{16}$. The infrared spectra, while consistent with the assigned structures do not provide essential information beyond a band at 1654 cm^{-1} which indicates the presence of a double bond in a six-membered ring.[11] The nmr spectra which were expected to be definitive, appeared initially discouraging. Compound 5 had the "proper" spectrum, but 4 did not. The spectrum of 5 consists of a two-proton multiplet at τ 4.6 (olefinic hydrogens), a four-proton multiplet at τ 7.8 (methylene hydrogens), a broad two-proton multiplet at τ 8.7-8.9 (bridgehead hydrogens) a set of two overlapping doublets integrating for six protons (two non-equivalent methyl groups each split by a single adjacent hydrogen. The doublets are overlapping at 60 MHz but distinct at 100 MHz), and a two-proton multiplet at τ 9.3-9.4 (cyclopropyl hydrogens). The *cis*-compound 4 shows a very similar spectrum except that the overlapping doublets and the highest field multiplet are replaced with a sharp singlet at τ 9.0 which integrates for eight protons. Spectra taken in carbon tetrachloride, chloroform, acetone and dimethylsulfoxide show no important changes. The mystery is resolved, however, when the spectrum is obtained in benzene. The singlet is split into two lines. The cyclopropyl hydrogens are still not resolved but at least the two methyl groups appear. The set of coincidences necessary to render two intrinsically non-equivalent methyl groups equivalent to each other and to two other intrinsically non-equivalent hydrogens as well seems most remarkable to us. Similar, if not quite as extensive coincidences seem to have been noticed before in related spiro systems.[12,13]

Treatment of 4 and 5 with molecular bromine in methylene chloride proceeded smoothly to give two uncharacterized dibromides which could be dehydrobrominated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in acetone at 100° to give the spirononatrienes 1 and 2 in 15% yield.

The elemental compositions of these sensitive compounds were determined by high resolution mass spectroscopy.[14] As before, the infrared spectra were consistent with the assigned structures but not decisive. In both 1 and 2 there is a low field pattern in the nmr at τ 3.5-4.2 (four hydrogens) along with a two-proton signal at slightly higher field, τ 4.8-5.1. This is very similar to the spectra described by W. M. Jones.[7] The up-field portions of the spectra reveal coincidences similar to those found in the precursors. Again the trans-compound is "normal" having a methyl doublet at τ 8.95 and a two-proton multiplet at τ 9.6. The cis-compound 1 has only an eight proton singlet at τ 9.16.

The small external angle in 1 and 2 allows the anticipation that these compounds will be far towards the cycloheptatriene side of the norcaradiene-cycloheptatriene equilibrium. Closing to the norcaradiene involves building a spiropentane and this is strongly resisted. The small external angle resists closing the internal angle. The spectra of 1 and 2 as well as those of W. M. Jones' compounds indicate that this is so. A precise determination of the equilibrium constant awaits low temperature nmr work, but the chemical shift of the hydrogens in the 4 and 9 ring positions requires that not much of the norcaradiene form can be present.

REFERENCES AND NOTES

(1) This work is taken from the Thesis of E. W. P., Jr., submitted in partial fulfillment of the requirements for the A.B. degree at Princeton University. Presented in part at the 23rd Eastern Colleges Scientific Conference, New Haven, Connecticut, April, 1969.

(2) Alfred P. Sloan Research Fellow, 1967-9.

(3) For a review see: G. Maier, *Angew.Chem.*, **79**, 446 (1967).

(4) M. Jones, Jr., *J.Org.Chem.*, **33**, 2538 (1968). See also: D. M. Gale, *ibid.*, **33**, 2536 (1968).

(5) M. Jones, Jr., *Angew.Chem.*, **81**, 83 (1969). See also: D. Schönleber, *ibid.*, **81**, 83 (1969).

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(8) W. R. Moore and H. R. Ward, *J.Org.Chem.*, **25**, 2073 (1960).

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(14) We thank the National Science Foundation for help towards the purchase of the AEI-MS-9 Mass Spectrometer through Grant GP-5200. The Instrument Laboratory at Princeton is supported in part by Biomedical Sciences Support Grant FR-07057.